**RSTDPT (Harmonic Perturbation)**

Now want to do some examples,

**Example. Atomic Transition Rules**

Let’s consider an EM wave interacting with a hydrogen atom. We’ll recall that the Hamiltonian for particles interacting with EM fields is.



where A(r,t) is the vector potential, and φ(r,t) the scalar potential associated with the EM field. And recall the electric/magnetic field is given by:



There are many options to describing an EM wave. Let’s use the temporal gauge (see EM folder/Free Maxwell Equations TD). This gauge is described by:



So in a source free region, the temporal gauge equations are:



The last equation is the wave equation, and its solution is obviously,



So this is our plane wave. And the associated EM field would be given by:



Note that in order to satisfy the gauge condition (∂/∂t)∇·**A** = 0, we’ll need to make ∇·**A** = 0 itself, which implies **k**·**A**0 = 0. Now let’s expand our Hamiltonian to first order in the perturbation (**A**),



(always implicitly taking the real part of any wave) Now note that in the **p**·**A** term, the **p** operator is acting both on **A**, and on any ket that appears to the right of **A**. But since ∇·**A** = 0 means we can slide the **p** past the **A**, combine with the preceding term, and write:



We should be able to neglect the position dependence of A(r). For a typical wave that would induce transitions, we can say that its photon energy should be on the order of the hydrogen atom ground state energy. So,



where a0 is the Bohr radius. So the size of the wave would be:



filling in the Bohr radius a0 to the term in parentheses,



where we recognize the fine structure constant α



So….λ ~ 4π(137)a0, which is much larger than a0, which is the size over which the electron in an atom will roam. So we can safely neglect the spatial dependence of the EM wave. Now let’s consider transitions between different atomic eigenstates |i> = |nℓm> --> |n> = |n´ℓ´m´>. We can use:



(we’re missing the factor of 2 in front of the π because it is canceled by the ½ coming from cos(ωt) = (1/2)(eiωt + e-iωt) in A(r,t)) We only have to evaluate:



To help evaluate the matrix element, we use following trick,



So,



which is easier (can replace En – Ei w/ ω thanks to the δ function in Γ) …so now we need to evaluate:



Now consider <n||i> from a general vantage point. And recall that is a 1st rank spherical tensor operator, and also odd under parity (see QM Foundations/Tensor Operators & Parity Symmetry). So the only non-zero expectations that we’ll get from this require:



Here’s another perspective on why we can’t have transitions between states that don’t satisfy this equality. So if a photon comes along with frequency given by hf = ΔEni, where ΔEni is the energy difference between two atomic levels, and an electron is occupying one of those levels already, then the photon will ostensibly cause it to oscillate between the two levels, with angular frequency ωni = ΔEni/ℏ. But such a transition may be forbidden on energy conservation grounds. So classically, such an oscillating electron would give off dipole radiation according to (see EM folder):



(P is power) But if P = 0, because the matrix element = 0, then this transition would be forbidden on physical grounds/energy conservation violation. So consider an electron in a superposition state between the two levels:



where c1(t), c2(t) will both oscillate out of phase with each other (note this is basically the form the wavefunction would take when a harmonic perturbation is in resonance with the energy level difference). And let’s form the expectation of r.



The first two terms will be time-independent as c1 modulus squared will give a time-independent number, assuming it goes as c1 ~ exp(-iωnn′t). Therefore, it is only the cross term which will be time-dependent, and if there is to be radiation, then we must have this cross term to be non-zero. When will this happen? Consider the consequence of parity symmetry, first operating on the **r**, and then on the wavefunctions…



in order for these matrix elements to be 0, we must have that the prefactors don’t match, so we would have,



What does TRS say?



(where we note that |ℓ-m> is the complex conjugate of |ℓm>). Not sure what this says. This isn’t obviously wrong, so I would say TRS doesn’t say much here. What does rotational symmetry say? According to the spherical tensor stuff in QM/Foundations/Tensor Operators file, we would have,



But can see that parity forbids Δℓ = 0, since then ℓ+ℓ′ would be even, but the other is OK. So our transition rules would be:



Observe how this is precisely what we would expect (sans the negation of the Δℓ = 0 possibility) knowing that the photon has a spin of 1 and based our selection rules on conservation of angular momentum grounds.

**Example. Photoelectric Effect**

Let’s reprise our example above, but this time we’ll consider transitions where the electron is kicked out of the atom entirely. So the initial state|i> will be some |nℓm>, and the final state|n> will be some super high energy state of the atom, approximately equal to a plane wave |p>. Borrowing all of our work above, we have to evaluate:



where the matrix element is given by:



(we’re missing the factor of 2 in front of the π because it is canceled by the ½ coming from cos(ωt) = (1/2)(eiωt + e-iωt)) Let’s work this matrix element out, taking our initial state to be the hydrogen ground state. The hydrogen states are given by:



where,



So the ground state is, ignoring spin d.o.f.:



Our final state is some approximately free state. So then,



Can evaluate by aligning z-axis with **k**. Then we have:



Can simplify a little by saying,



Continuing on,



So our scattering rate is:



I think we’re most interested in the transition rate in a certain direction, irrespective of the speed. So let’s integrate over the magnitude of k, but keep the direction fixed. Also, presuming ω is positive, and since k2/2m > EGS, only the last delta function will matter. Also recall δ(f(x)-f(a)) = δ(x-a)/|f´(a)|. So,



which is:



We could find the probability distribution of scattering in the direction , within the cone dΩ. We just need to figure out the total scattering rate and divide our Γi→dΩ by that. So let’s align our z-axis with . Then we need to do:



So the probability of scattering at angle θ would be:



Maybe not the most informative measurement ever, since we’ve wiped out all the quantum mechanics of our result.

**Example. EM wave hitting a free electron**

It’s interesting to consider an EM wave impinging upon a free electron. What is the probability it will go from free state |**p**> to free state |**p**´>? Going back to our H,



And using the temporal gauge, as above, we can describe a wave via:



And then expanding our H out to first order in A,



Now let’s consider transitions between different free states, say |**p**> and |**p**´>. According to our QM, the rate of this transition for incomming evanescent EM wave is:



(we’re missing the factor of 2 in front of the π because it is canceled by the ½ coming from cos(ωt) = (1/2)(eiωt + e-iωt)) We’ll say ω is positive and p´ > p, for the sake of discussion. So then,



The matrix element is:



So our scattering rate is:



Important thing is that we have delta functions requiring conservation of energy and momentum. Turns out these two equations cannot be simultaneously satisfied though (see Particle Physics folder/Compton Effect, or Condensed Matter/Metals/Free Day/Non-equilibrium/Absorption). So free electrons cannot absorb photons apparently, though they can be scattered by them (Compton Effect).

**Example**

A nonrelativistic particle of mass m and charge q is confined to an infinite square well in three dimensions with sides of length Lx , Ly , and Lz in the x , y , and z directions, respectively. The particle has been undisturbed and in its ground state (nx,ny,nz)=(1,1,1) for all of time. Suddenly for a time T an electromagnetic wave passes through the box with wavelength λ . The wave is traveling in the y -direction and polarized in the z -direction and the electric field wave has amplitude E0 . What is the probability that at some time after the wave has passed the system will be found in state (nx,ny,nz)=(1,1,2)? Work to first order in perturbation theory and ignore terms in the Hamiltonian with vector potential squared. Also assume that the box is much smaller than the wavelength so that spatial variations of the electromagnetic field within the box at a given time can be ignored.

Well, our Hamiltonian is:



And using the temporal gauge, we can describe a wave via:



And then expanding our H out to first order in A,



Using,



And also accounting for the fact that E is polarized in the z-direction, we can write this as:



We’ll also ignore the spatial dependence, as instructed,



So then, our transition, to first order is governed by:



Let’s calculate the matrix element,



The eigenstates/energies of the unperturbed Hamiltonian are:



So,



Also have:



Filling these into our S formula,



So probability is:



Units,

